The University of Chicago

I. THE PEROXIDE EFFECT IN THE ADDITION OF HYDROGEN BROMIDE TO 1- AND 2-BROMO- AND CHLOROPROPENES

II. THE REACTION OF UNSATURATED HYDROCARBONS WITH SULFINIC ACID

A DISSERTATION SUBMITTED TO THE FACULTY OF THE DIVISION OF THE PHYSICAL SCIENCES IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1938

By
HELMUT M. ENGELMANN

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THE PEROXIDE EFFECT IN THE ADDITION OF HYDROGEN BROMIDE TO 1- AND 2-BROMO- AND CHLOROPROPENES

INTRODUCTION

The purpose of this investigation was twofold: first, to correlate the structures of ethylene compounds with susceptibility to the "peroxide effect"; second, to extend our knowledge of the intermediates formed in the addition of two moles of hydrogen bromide to methylacetylene under "antioxidant" and "peroxide" conditions.[1] Both objectives seemed attainable in a study of the addition of hydrogen bromide and hydrogen chloride to 1- and 2-bromo- and chloropropenes.

It has been established, by investigators in this laboratory and elsewhere, that excellent yields of either of the two possible products of the addition of one mole of hydrogen bromide to unsaturated compounds may be obtained with the following substances: propene[2], 1-butene[3], 2-methylpropene[4], 1-pentene[5], 4,4-dimethyl-1-pentene[6], 1-nonene[7], 1-undecene[7], 1-tridecene[7], 1-pentadecene[7], vinyl chloride[8], vinyl bromide[9], allyl bromide[10], allyl chloride[11], butadiene[12], vinylacetic acid[13], allylacetic acid[13, 14], undecenoic acid[15], ethyl undecenoate[16], undecenyl acetate[16], undecynoic acid[17], and butylacetylene[18]. It has not been possible, however, to alter

[1] KHARASCH, MCNAB, AND MCNAB, *J. Am. Chem. Soc.*, **57**, 2463 (1935).

[2] KHARASCH, MCNAB, AND MAYO, *ibid.*, **55**, 2531 (1933); KHARASCH AND MCNAB, *ibid.*, **56**, 1425 (1934); BROUWER AND WIBAUT, *Rec. trav. chim.*, **53**, 1001 (1934).

[3] KHARASCH AND HINCKLEY, *J. Am. Chem. Soc.*, **56**, 1212 (1934).

[4] KHARASCH AND HINCKLEY, *ibid.*, **56**, 1243 (1934); KHARASCH AND POTTS, *ibid.*, **58**, 57 (1936).

[5] KHARASCH, HINCKLEY, AND GLADSTONE, *ibid.*, **56**, 1642 (1934).

[6] KHARASCH, HANNUM, AND GLADSTONE, *ibid.*, **56**, 244 (1934).

[7] KHARASCH AND POTTS, *J. Org. Chem.*, **2**, 195 (1937).

[8] KHARASCH AND HANNUM, *J. Am. Chem. Soc.*, **56**, 712 (1934).

[9] KHARASCH, MCNAB, AND MAYO, *ibid.*, **55**, 2521 (1933).

[10] KHARASCH AND MAYO, *ibid.*, **55**, 2468 (1933).

[11] SHANE, Ph.D. Dissertation, University of Chicago, **1933**.

[12] KHARASCH, MARGOLIS, AND MAYO, *J. Org. Chem.*, **1**, 393 (1936).

[13] LINSTEAD AND RYDON, *J. Chem. Soc.*, **1934**, 2001.

[14] KHARASCH AND MCNAB, *J. Soc. Chem. Ind.*, **54**, 989 (1935).

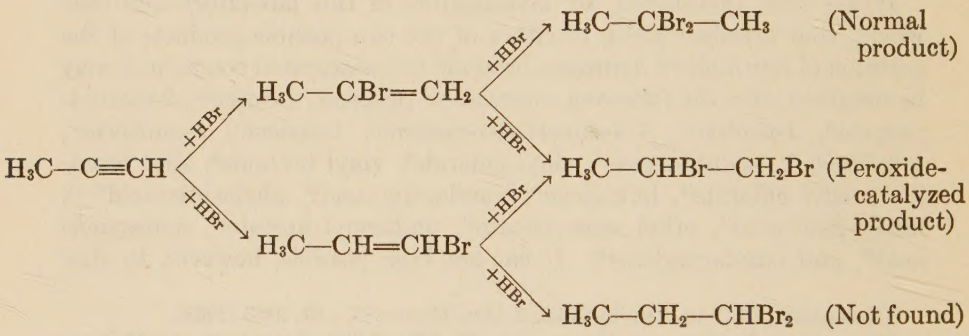
[15] ASHTON AND SMITH, *J. Chem. Soc.*, **1934**, 435.

[16] ASHTON AND SMITH, *ibid.*, **1934**, 1308.

[17] HARRIS AND SMITH, *ibid.*, **1935**, 1572.

[18] YOUNG, VOGT, AND NIEUWLAND, *J. Am. Chem. Soc.*, **58**, 1806 (1936).

the relative proportion of addition products from 2-pentene[19] or undecylenic acid[20] by the use of antioxidants or peroxides, or to obtain more than one product with styrene[21], propenylbenezene[22], undecenol[16], acrylic acid[23], bromomaleic acid[23], bromofumaric acid[23], bromocrotonic acid[23], crotonic acid[23]. A study of the structures of the compounds known to show a "peroxide effect" discloses that they all have a terminal double bond. Obviously, it is of importance to determine whether the presence of two hydrogen atoms on the terminal carbon atom is essential, or whether one of them may be replaced by another atom, such as a halogen atom. Incidentally, a study of the addition of hydrogen bromide to chloro- and bromopropenes not only answers this question, but may be of value in the determination of the intermediate product in the addition of two moles of hydrogen bromide to methylacetylene[1] in the presence of peroxides, as can be seen from the following schematic representation of the reaction.



PREVIOUS WORK

2-Bromo- and 2-chloropropene and the cis and trans forms of 1-chloro- and 1-bromopropene have been described, and some of their physical constants have been recorded. Reboul[24] is the only author who has reported the addition of hydrogen bromide to these unsaturated compounds. However, the conclusions he draws from his experimental data are open

[19] Kharasch, Hinckley, Beck, and Mayo, unpublished work.
[20] Harris and Smith, *J. Chem. Soc.*, **1935**, 1108.
[21] Kharasch, Mayo, and Hammond, unpublished work.
[22] Kharasch and White, unpublished work.
[23] Kharasch and McNab, unpublished work.
[24] Reboul, *Ann. chim.*, [5], **14**, 453 (1878).

to serious objection. Thus, he records that 1-bromopropene, when treated with four to five volumes of saturated aqueous hydrobromic acid, yields a dibromide. From the fact that the dibromide boiled over a wide temperature range (8°), he assumed that it was a mixture of 1,2- and 1,1-dibromopropane, with a predominance of the former product. He was unable, however, to isolate any pure 1,1-dibromopropane from the reaction mixture, though he predicts that the compound would boil at 131–3°. However, a critical examination of the data suggests that the low-boiling compound obtained by Reboul in the above addition was not 1,1-dibromopropane, but 2,2-dibromopropane. Reboul prepared his 1-bromopropene by treating a mixture of 1- and 2-bromopropene with hydrogen bromide. The method depends upon the observation that the 2- derivative adds hydrogen bromide faster than the 1- compounds. A mixture rich in the 1- form could thus be obtained, and Reboul considered the substance to be pure 1-bromopropene when the boiling point of the material did not change upon further treatment with hydrogen bromide. It is evident, however, that the material must contain a mixture of 1- and 2-bromopropene in quantities approximately inversely proportional to their reactivities. His evidence that 1,1-dibromopropane is formed by the addition of hydrogen bromide to 1-bromopropene is therefore inconclusive.

Reboul records that when a concentrated aqueous solution of hydrogen bromide is added to 2-bromopropene, 2,2-dibromopropane is formed exclusively.

Reboul also studied the addition of concentrated aqueous hydrobromic acid to 1- and 2-chloropropene. He states that 1-chloropropene yielded a mixture of products, but that 1-bromo-1-chloropropane predominated, and that only a small amount of 1-chloro-2-bromopropane was formed. In this case, the criticism of the purity of the initial material is perhaps not valid, for the 1-chloro compound is reported to have been prepared from 1,1-dichloropropane, and should therefore be free from isomers. Careful perusal of Reboul's paper, however, fails to yield any satisfactory proof that his addition product was pure.

Reboul claims to have obtained 2-bromo-2-chlorpropane exclusively by addition of hydrogen bromide to 2-chloropropene.

ADDITION OF HYDROGEN BROMIDE TO BROMO- AND CHLOROPROPENES UNDER "PEROXIDE" AND "ANTIOXIDANT" CONDITIONS

As is recorded in Table I, the "normal" product of the addition of hydrogen bromide to 2-bromopropene is 2,2-dibromopropane. This product is formed *in vacuo* in the presence of "antioxidants". The fact

TABLE I

THE ADDITION OF HYDROGEN BROMIDE TO 2-BROMOPROPENE

EXPT. NO.	MOLES[a] HBr	PEROXIDE OR ANTIOXIDANT, MOLES[a]	TECHNIQUE	REACTION TIME AT ROOM TEMP.	YIELD[b]		% 2, 2- ADDITION PRODUCT[c]	REMARKS
					Minimum, %	Estimated, %		
2	1.5	None	Air, 1	20 hours		100	96	Estimated from b.p.
15	2.1	None	Air, 1	28 hours	75		85–90	
13	1.7	Ascaridole, .06	Air, 2	5 hours	79		17	Checked
33	1.5	Ascaridole, .08	Air, 8	6 hours		81	17	
5	1.5	Diphenylamine, .03	Vacuum, 1	44 hours		100	100	
34	1.5	Diphenylamine, .04	Vacuum, 8	27 hours		92	99	
16	1.5	Thiophenol, .04	Vacuum, 2	21 days	42		98	

[a] On basis of halogenated propylene used.

[b] The "minimum yield" is calculated from the weight of pure dihalide mixture isolated after the final distillation. Low yields are often due to losses from incomplete condensation in vacuum distillations. "Estimated yields" are based on the weight of crude reaction product after removal of solvent, catalyst and hydrogen bromide, or on the presence or absence of unreacted halogenated propylene.

[c] Remainder was other possible addition product.

TABLE II

THE ADDITION OF HYDROGEN BROMIDE TO 2-CHLOROPROPENE

EXPT. NO.	MOLES[a] HBr	PEROXIDE OR ANTIOXIDANT, MOLES[a]	TECHNIQUE	REACTION TIME AT ROOM TEMP.	YIELD[b]		% 2, 2- ADDITION PRODUCT[c]	REMARKS
					Minimum, %	Estimated, %		
58	1.5	None	Air, 1	41 hours	92	100	100	Checked
83	1.7	Ascaridole, .06	Air, 8	7 hours	86	<100	26	
54	1.5	Ascaridole, .02	Air, 3	9 days	71	100	18	
60	1.5	Benzoyl peroxide, .01	Air, 1	5 hours	98		82	
82	1.5	Diphenylamine, .03	Vacuum, 6	40 hours		70	100	
56	1.5	Diphenylamine, .03	Vacuum, 3	7.5 days	43	100	100	

[a, b, c] Have the same significance as in Table I.

that the same product is formed in air, and in the presence of the small amounts of peroxides, formed from the unsaturated compound and oxygen, indicates that this reaction is not particularly sensitive to small amounts of peroxides. However, in the presence of an added peroxide (ascaridole) 80 to 90 per cent. of 1,2-dibromopropane is readily obtained.

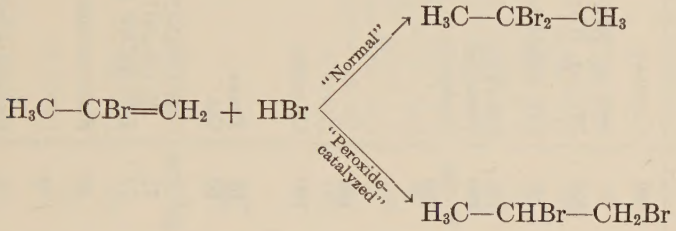


Table II shows that the behavior of 2-chloropropene towards hydrogen bromide is in all respects similar to that of 2-bromopropene. In the presence of air, or in the presence of antioxidants *in vacuo*, the product is pure 2-bromo-2-chloropropane. When an organic peroxide is added to the reaction mixture, 1-bromo-2-chloropropane is the major reaction product. It is of considerable importance that even the "normal" addition of hydrogen bromide to either 2-bromo- or 2-chloropropene is comparatively rapid, and usually complete within a day or two.

The results of addition of hydrogen bromide to the 2-halopropenes are thus in accord with our previous experience and theoretical predictions. The situation is much more complicated in the case of addition of halogen acids to the 1-halopropenes. Here significant differences have been observed in the case of the 1-chloro and 1-bromopropene. In view of the precautions taken in this work the differences observed cannot be dismissed as consequences of experimental error. We believe rather that they have an important and significant theoretical background. It is easy to perceive, on the basis of the hypothesis developed by Kharasch and collaborators, that in the 2-halopropenes, insofar as electron distribution at the double bond is concerned, that both the methyl groups and the halogen atoms tend to produce a similar electronic distribution, and their individual effects thus reinforce each other. In the 1-halopropenes, there is a distinct opposition of the two effects, and, we believe that the differences observed with 1-chloro- and 1-bromopropene find their explanation in the relative effectiveness of these halogen atoms when in opposition to a methyl group.

Tables III and IV record our observations of the addition of hydrogen bromide to 1-chloro- and 1-bromopropene, respectively. We ordinarily used mixtures of the *cis* and *trans* forms of these halides, but in the tables

TABLE III

The Addition of Hydrogen Bromide to 1-Chloropropene

Expt. No.	Moles[a] HBr	Peroxide or antioxidant, moles[a]	Technique	Reaction time[d]	Yield[b] Minimum, %	Yield[b] Estimated, %	% 1,2-addition product[c]	Remarks
57	1.5	None	Air, 1	41 hours	95	100	100	Checked.
67	2.0	None	Air, 4*b*	6 months		<5		42% aq. HBr.
66	1.8	None	Air, 4*b*	5 days	60		100	70% aq. HBr, checked twice.
97	1.54	None	Vac., 9	68 hours	85	90	98	*Cis;* complete in 2 days.
72	1.5	Ascaridole, .05	Air, 6	1 hour		21	100	Checked.
78	1.5	Ascaridole, .025	Air, 7	24 hours		98	100	Checked.
95	1.58	Ascaridole, .03	Air, 9	19 hours	61		90–100	Complete in 1 hour.
59	1.5	Bz_2O_2, .015	Air, 1	5 hours	90		100	
76	1.5	Ph_2NH, .025	Vac., 6	24 hours		3		
79	1.5	Ph_2NH, .03	Vac., 8	4 days		24		
55	1.5	Ph_2NH, .025	Vac., 2	7 days	53		100	
63	1.5	Catechol, .04	Vac., 3	23 hours	86	100	100	Checked
80	1.5	PhSH, .035	Vac., 6	24 hours		6		
96	1.56	PhSH, .045	Vac., 9	40 days	57	65	67	*Trans*
102	1.59	PhSH, .045	Vac., 9	36 days	65	70	63	*Cis*
94	1.61	PhSH, .06	Vac., 9	67 hours	29		35 ±10	.34 *t*-BuNC[a] added.
100	1.54	PhSH, .05	Vac., 9	9.5 days	66	79	71	.18 *t*-BuNC added.
99	2.01	PhSH, .05	Vac., 10	10.5 days	84	88	79	1.00 AcOH[a] added.
98	2.01	EtSH, 1.00	Vac., 9	10.5 days	54		56	Side-reaction.
93	1.58	Anh. $FeCl_3$, .006	Vac., 9 (0°)	2 hours	83	96	8	
101	1.65	Anh. $FeCl_3$, .003	Vac., 9 (0°)	2 hours	15			
103	1.55	Anh. $FeCl_3$, .018	Vac., 9 (0°)	13 hours	91		5	Complete in 8 min.
	Moles HCl							
90	2.0	Anh. $FeCl_3$, .04	Air, 6	2 days		90	90–100	Checked twice.

[a, b, c] Have the same significance as in Table I.
[d] At room temperature except in last three experiments.

TABLE IV

The Addition of Hydrogen Bromide to 1-Bromopropene

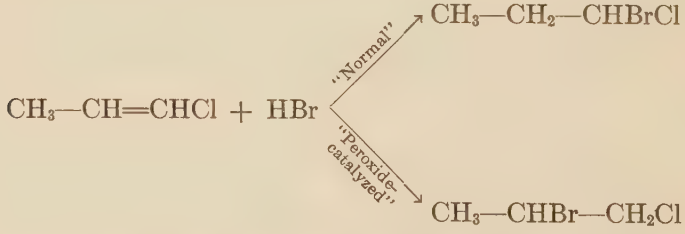
Expt. No.	Moles[a] HBr	Peroxide or Antioxidant, Moles[a]	Technique	Reaction Time[d]	Yield[b] Minimum, %	Yield[b] Estimated, %	% 1, 2-Addition Product[c]	Remarks
1	1.5	None	Air, 2	20 hours			100	
35	7.5	None	Air, 4*b*	2 months	70		100	65% aq. HBr.
14	2.5	Ascaridole, .04	Air, 2	3 hours	84		100	Checked.
3	1.5	Bz_2O_2, .02	Vac., 1	20 hours			100	
39	3.0	None	Air, 5*b*	5 days	70		100	2.0 H_2O — 0.02 $FeCl_3 \cdot 6H_2O$ added[a].
30	1.5	Ph_2NH, .04	Vac., 8	19 days		62	100	Checked.
25	1.5	$FeSO_4 \cdot 7H_2O$, .07	Vac., 4*a* (0°)	39 hours	70		100	
26	1.5	Ph_2NH, .04 $FeSO_4 \cdot 7H_2O$, .07	Vac., 2 (0°)	41 hours	70		100	
31	1.5	PhSH, .04	Vac., 6	24 hours		5		
18	2.0	PhSH, .04	Vac., 2	5 months	75	100	100	Checked.
41	1.59	PhSH, .04	Vac., 9	18 days	90	91	97	*Trans;* complete in 10 days.
42	1.50	PhSH, .04	Vac., 9	18 days	83	91	97	*Cis;* complete in 14 days.
9	2.4	PhSH, .04	Vac., 4*a*	88 hours	60		100	1.0 AcOH added[a], checked.
43	2.03	PhSH, .04	Vac., 10	11 days	93		99	*Cis;* 1.0 AcOH added.
48	2.19	PhSH, .04	Vac., 10	8 days	93		99	1.0 AcOH added.
20	2.0	PhSH, .04	Vac., 2	4½ days	80		100	0.2 EtCN added[a].
21	2.0	PhSH, .04	Vac., 2	4½ days	80		100	0.2 MeNC added.
45	1.53	PhSH, .04	Vac., 9	13 days	88	98	92	0.15 *t*-BuNC added; complete in 8 days.
38	2.0	*p*-MeC_6H_4SH, .05	Vac., 8	6 days	70		100	0.5 *t*-BuNC added.
44	1.74	EtSH, .50	Vac., 9	9 days	63		94	Side-reaction.
40	1.62	Anh. $FeCl_3$, .006	Vac., 9 (0°)	2 hours	90	95	67	
47	1.52	Anh. $FeCl_3$, .01	Vac., 9 (0°)	45 min.	91		67	Complete in 5 min.
	Moles HCl							
49	1.62	Anh. $FeCl_3$, .016	Vac., 9 (0°)	15 hours	61	95	65	Complete in 4 hours.

[a, b, c] Have the same significance as in Table I.
[d] At room temperature except as noted.

we include a few experiments in which the pure geometrical isomers were used without significant differences in the results.

In the presence of air and/or added peroxides, 1-chloropropene adds hydrogen bromide rapidly to give 1-chloro-2-bromopropane exclusively. In the absence of air, the addition is slower, but the product is the same. The first experiments *in vacuo* with antioxidants gave the same results, but the reaction appeared to proceed at a still slower rate. The implications involved in this decrease in rate of addition under antioxidant conditions were clear to us, and in experiments 96 and 102 extreme precautions were taken to exclude oxygen and/or peroxides. We also used freshly prepared 1-chloropropene. Under such strict "antioxidant" conditions the rate of addition is exceedingly slow. Thus, in 36 to 40 days, only about 60 to 75 per cent. of the 1-chloropropene reacted to give an addition product of which about one-third was 1,1- and two-thirds was 1,2-dihalopropane. Approximately the same addition mixture, however, can be obtained in a shorter time in the presence of substances which have been shown to accelerate the "normal" addition of hydrogen bromide; *e.g.*, glacial acetic acid[10], or tertiary butyl isocyanide.[9] The use of ethyl mercaptan as a combined solvent and antioxidant gave an accelerated addition and still more 1,1-dihalide, but with the complication of a side reaction mentioned in the experimental part. The last three experiments with hydrogen bromide in Table III show that in the presence of anhydrous ferric chloride (which thus far[9,10] is known to catalyze only the "normal" addition of hydrogen bromide), and in the absence of air, more than 90 per cent. of the 1,1-dihalide is obtained in a few minutes at 0°.

These results suggest that the "peroxide-catalyzed" addition of hydrogen bromide to 1-chloropropene yields 1-chloro-2-bromo-propane exclusively, and that the "normal" addition yields 1-chloro-1-bromopropane. However, the "normal" addition is so slow that it has thus far been impossible to eliminate completely the "peroxide-catalyzed" reaction. We believe, however, that higher yields of the "normal" product, than recorded by us, can be obtained by a more rigorous exclusion of oxygen and/or peroxides.



In substantiation of our conclusion as to the course of the "normal" and "peroxide-catalyzed" reaction with 1-chloropropene, we may cite our

experience with the addition of hydrogen chloride to this substance. No peroxide effect has ever been observed with hydrogen chloride[25], and complications from that source are thus eliminated. Unfortunately, hydrogen chloride does not add to 1-chloropropene at an appreciable rate at ordinary temperatures. In the presence of ferric chloride, however, a rapid reaction takes place even at 0°. In three experiments we obtained, within the limits of error of our analytical method, the 1,1-dichloropropane exclusively. We believe, that in this instance the function of the ferric chloride is to accelerate the "normal' adddition, a conclusion justified by our past experience in the use of this reagent as a catalyst in addition reactions.

The results of addition of hydrogen bromide and hydrogen chloride to 1-bromopropene are recorded in Table IV. As mentioned before, the interpretation of these data is much more difficult, but the implications have great interest.

In the absence of air and in the presence of ferric chloride at 0°, 1-bromopropene adds hydrogen bromide in a few minutes to give a mixture of one-third 1,1-dibromopropane and two-thirds 1,2-dibromopropane. *In vacuo* and in the presence of antioxidants, up to 8 per cent. of 1,1-dibromopropane is obtained in the presence of accelerators of the reaction. The latter result is close enough to our admitted experimental error to be of doubtful significance. Under all other conditions, the only addition product obtained was 1,2-dibromopropane, but, as with 1-chloropropene, removing air and adding antioxidants greatly decreased the rate of reaction. We have thus no indication that the normal addition of hydrogen bromide to 1-bromopropene would give more 1,1-dibromide than was obtained in the ferric chloride experiments (33 per cent.). On the contrary the results with antioxidants indicate that this may be the limiting amount of 1,1-dihalide obtainable in the absence of ferric chloride and air, as the peroxide effect is eliminated more completely than has yet been found possible. As a further check of this assumption, we investigated the addition of hydrogen chloride to 1-bromopropene in the presence of ferric chloride at 0°. While, in the case of 1-chloropropene a quantitative yield of the 1,1-dichloropropane was obtained, the 1-bromopropane yielded a mixture of the 1,1 and 1,2 isomers, in an approximate ratio of 1 to 2, respectively. It is to be noted that the same ratio was obtained in the addition of HBr to the 1-bromopropene in the presence of ferric chloride.

For ease of comparison, the behavior of the 1-bromo- and 1-chloropropenes with different reagents is summarized in Table V.

The interpretation of the results recorded in Table V is a matter of

[25] Kharasch and Mayo, unpublished work; Abraham and Smith, *J. Chem. Soc.*, **1936**, 1605.

considerable importance. We believe it is established now beyond a reasonable doubt that for each halopropene there is a "normal" and "abnormal" addition, the latter catalyzed by peroxides, and that the composition of the product can readily be controlled by a proper appreciation of these factors. One is forced to admit, therefore, a striking difference in behavior toward halogen acids of the 1-chloro- and 1-bromopropenes. The difference is intimately connected with the general question of formation of two products as a result of a "normal" addition of a halogen acid to an unsaturated molecule. Furthermore, as has been already pointed out by Kharasch and Reinmuth[26], the only substituted ethylene compounds which show this behavior are those in which the two opposing groups are about equal in electronegativity. The striking difference toward halogen acids of the 1-chloro- and 1-bromopropenes may thus be readily accounted for. The broad general problem, however, of

TABLE V

SUMMARY OF THE ADDITION OF HYDROGEN BROMIDE AND HYDROGEN CHLORIDE TO 1-CHLORO- AND 1-BROMOPROPENES

HALOGEN ACID ADDED	CONDITIONS	% 1, 1-DIHALIDE FROM 1-HALOPROPENE*	
		Chloro-	Bromo-
HBr	Peroxides and/or air present.	0	0
HBr	Air absent, antioxidant present.	20–60	0–10
HBr	Air absent, $FeCl_3$ catalyst.	90–100	33
HCl	$FeCl_3$ catalyst.	90–100	35

* The remainder was the other possible addition product (1,2-).

the significance of the formation of two products as a result of a "normal" addition remains unanswered. As we perceive it, there are numerous verbalistic variations of the speculative interpretations of this phenomenon that may be offered. If mechanistic details are omitted, however, they would all seem to be reducible to two alternatives. Either (*1*) such compounds exist in a dynamic equilibrium of two forms*, or (*2*) in one form in which the double bond is so slightly polar that the energy changes involved in addition in either direction are nearly equal (as they are presumably exactly equal for such symmetrical molecules as ethylene itself).

[26] KHARASCH AND REINMUTH, *J. Chem. Educ.*, **8**, 1703 (1931).

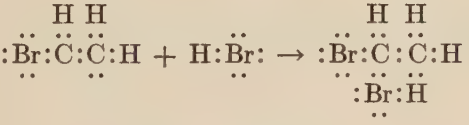
* A consequence of this assumption is that one form "normally" adds halogen acids to give the 1,1-dihalopropane and is susceptible to a "peroxide effect", the other "normally" gives the 1,2- isomer, and is not susceptible to a "peroxide effect" except for acceleration without reversal of addition.

The implications involved in these ways of viewing the facts are obvious and thought-stimulating, but speculations concerning them can lead nowhere, without further experimental evidence.

MECHANISM OF THE PEROXIDE EFFECT

Our tentative hypothesis of the nature of this effect is presented at this time in response to urgent requests of many investitators. In accounting for the remarkable effect of peroxides (and/or oxygen) on the nature of addition of hydrogen bromide to unsaturated molecules, it is important to bear in mind that no reversal has been obtained for hydrogen chloride[25] or sulfuric acid.†,[27]

To explain this "abnormal" effect it is necessary to dwell for a moment upon the normal reaction. In an earlier article by Kharasch and Reinmuth[26] it was postulated that in an unsaturated molecule of the type R—CH=CH_2 the "extra" electron-pair of the double bond would be displaced away from the carbon atom carrying the most electronegative radicals. A highly schematic representation of the "normal" addition of hydrogen bromide to vinyl bromide according to this hypothesis is given below.



This representation in the light of what we now know of the "peroxide effect," is in much better agreement with the facts than the one advanced by Lucas[28] and also by Robinson[29]. It is of interest to note that the chemically important essentials of the formulation are contained in the resonance formulae of the chloroethylenes postulated by Pauling, Brockway, and Beach.[30]

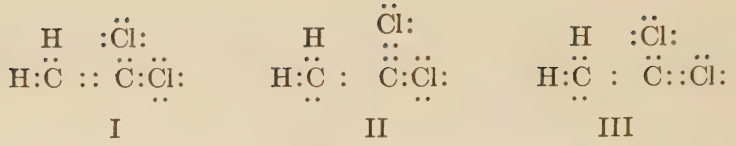
† The possibility of a peroxide effect in case of the other reagents mentioned in our first article[10] is still under investigation in this laboratory, as well as a further study of the addition of hydrogen iodide to unsaturated derivatives, under conditions which would be most likely to effect reversal.

[27] Kharasch and Klaas, unpublished work; Brooks, *J. Am. Chem. Soc.*, **56**, 1998 (1934).

[28] Lucas and Jameson, *J. Am. Chem. Soc.*, **46**, 2475 (1924).

[29] Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," The Institute of Chemistry of Great Britain and Ireland, London, **1932**.

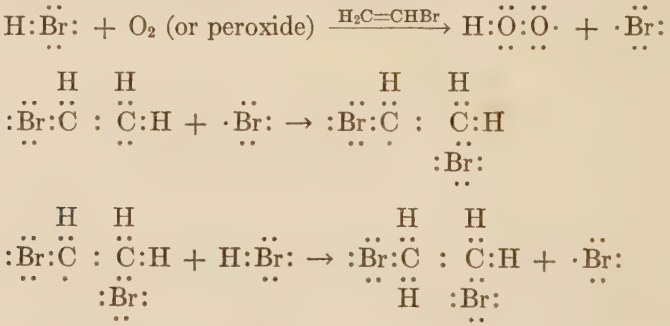
[30] Pauling, Brockway, and Beach, *J. Am. Chem. Soc.*, **57**, 2693 (1935).



I II III

These authors interpret their electron diffraction data on the dichloroethylenes in terms of resonance of the double bond among three possible positions in which the relative time spent in each position can be determined from the percentage of double (14 per cent.) and single (86 per cent.) carbon-to-chlorine bonds. Forms II and III are richer in energy than I. It is clear that although our notations are different, as would be expected of systems designed to interpret different phenomena, we arrive at essentially similar electronic structures for the terminal carbon atoms of the reactive forms of the haloethene molecules.

The effect of "peroxides" on the addition of hydrogen bromide to such an unsaturated molecule may be described by the following highly schematic representation.



The essential features of these representations are that, in the addition of hydrogen bromide to vinyl bromide under "antioxidant" conditions, the *bromide ion* is directed toward the carbon atoms with the lowest electron density to yield 1,1-dibromoethane, and that under "peroxide" conditions the *bromine atom* is directed toward the carbon atom with the greater electron density to yield a 1,2-dibromoethyl free radical. This free radical then reacts with hydrogen bromide to yield 1,2-dibromoethane and another bromine atom, which is responsible for the propagation of the chain reaction. According to this mechanism, the function of peroxides or oxygen is to initiate a chain reaction which supplies bromine atoms. Upon the basis of this mechanism it is easy to understand why there is no "peroxide effect" in the addition of hydrogen chloride or sulfuric acid to unsaturated molecules.

EXPERIMENTAL

Preparation of halopropenes.—1- and 2-Bromopropenes were prepared by the reaction between propylene bromide and alcoholic sodium ethylate. The product was washed with ice-cold 1-molar sulfuric acid, and with cold water, then dried with calcium chloride. The product was then distilled through a 1-meter column filled with glass beads. The constants obtained are listed in Table VI. Only a portion of the 1-bromopropene was resolved into the *cis* and *trans* forms.

1- and 2-Chloropropenes were prepared similarly from propylene chloride. The halopropenes were then isolated by distillation through a Podbielniak[31] column. This column could effect a separation of the *cis*- and *trans*-1-halopropenes, but most of the 1-halopropenes were used as mixtures in the proportions in which they were found. The constants obtained are listed in Table VI.

Preparation and analysis of reaction mixtures.—The techniques used in the addition of hydrogen bromide to the halogenated propylenes were those described by Kharasch and Mayo[10] for air and vacuum experiments. In general, 0.05 mole of bromopropene or 0.8 mole of chloropropene was used in each experiment, except that 0.1 of the unsaturated compound was usually employed when the product was to be distilled through the Podbielniak Column. At the proper time, the bomb tubes were cooled at about −80°, opened, and allowed to warm up to room temperature to permit escape of the free hydrogen bromide. Several procedures were used in working up the addition products. The numbers correspond to those used in Tables I–IV. (*1*) Products were distilled directly at atmospheric pressure. (*2*) Products were distilled first at 20–30 mm., then at atmospheric pressure. (*3*) Products were warmed in bomb tube to determine whether any unsaturated compound remained, then distilled at atmospheric pressure. (*4*) Products were poured into ice water, washed with water, dilute sodium bicarbonate, and twice more with ice water. The washed product was then dried over (*a*) calcium chloride or (*b*) sodium sulfate, and distilled at 20–30 mm. pressure. (*5a* and *b*) Same as *4a* and *b* except that products were distilled at atmospheric instead of reduced pressure. (*6*) Bomb tube containing products evacuated to about 50 mm. at 0° and shaken to remove unsaturated compound and halogen acid; product weighed to determine yield, then distilled at 10 mm. (*7*) Same as *6*, but washed with water and dried with Na_2SO_4 after weighing and before final distillation. (*8*) Same as *6*, but distilled at atmospheric pressure. (*9*) Product distilled at 20 mm. pressure and then fractionally distilled through Podbielniak column at 50 mm. or 75 mm. (*10*) Products poured onto ice, washed with water and cold bicarbonate solution, dried over anhydrous potassium carbonate and distilled through Podbielniak column as in *9*.

The unsaturated compound was removed from the addition product in the above distillations, and the composition of the addition product was determined by index of refraction with an Abbé refractometer. The boiling point observed in the distillation served to check the latter observation. We estimate the precision of the "estimated yield" and composition of the addition product at ±5%. This yield is thus a "minimum yield" while the actual yield might have been close to 100% when no "estimated yield" is given. See note (*b*), Table I. In some experiments, the rate of addition was measured roughly by the volume decrease of the reaction mixture, which amounted to about 12% at −80° for 100% addition, using about 1.5 moles of

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[31] Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **5**, 119 (1933).

hydrogen bromide and no solvent. When such measurements furnished additional information, the conclusions are mentioned in the remarks columns of the tables.

Isolation of pure addition products.—Near the completion of the above work, the appropriate addition products were combined and distilled through a Podbielniak column in order to isolate and determine the physical constants of pure samples of

TABLE VI

PHYSICAL CONSTANTS OF HALOGENATED PROPENES AND PROPANES

HALIDE	THIS PROJECT			LITERATURE					
	B. p., °C.	Pressure, mm.	n_D^{20}	B. p., °C.	Pressure, mm.	Reference	n_D	Temp., °C.	Reference
1-Br-propene (cis)	58.6– 58.7	748	1.4544	57.8	760	*32*	1.4564	16.2	*32*
1-Br-propene (trans)	64.2– 64.4	748	1.4532	63.25	760	*32*	1.4549	15.75	*32*
2-Br-propene	48.4	748	1.4440	48.35	760	*32*	1.44665	15.75	*32*
1-Cl-propene (cis)	32.0– 32.2	744	1.4055	32.8	760	*35*			
1-Cl-propene (trans)	36.7	747	1.4054	37.4	760	*35*			
2-Cl-propene	21.7– 21.8	743	1.3949	22.6	760	*35*			
1,1-di-Br-propane	135.3–135.7	740	1.5100	131–133		*24*			
	57.6– 57.8	50		(estimated)					
1,2-di-Br-propane	140.7–140.8	740	1.5200	140	760	*33*	1.5203	20	*33*
	61.8	50							
2,2-di-Br-propane	114.2–114.4	740	1.4988	114.0–114.5	740	*24*	1.4977	20	*1, 34*
	38.4– 39.4	50							
1-Br-1-Cl-propane	111.7–112.0	740	1.4703	110–112	760	*24*			
	47.8	75							
1-Br-2-Cl-propane	117.6–118.0	740	1.4778	117.5–117.8	756	*36*	1.47449	20	*36*
	52.2– 52.8	75							
2-Br-1-Cl-propane	117.2–117.3	740	1.4795	117.5–118.0	756	*36*	1.47447	20	*36*
	52.0	75		115–117	746	*11*	1.4795	20	*11*
2-Br-2-Cl-propane	91.0– 91.2	740	1.4575	93.0– 93.5	745	*24*			
	34.6– 34.8	100							
1,1-di-Cl-propane	87–88	750	1.4295	87	760	*33*			
1,2-di-Cl-propane				96.8	760	*33*	1.4388	20	*33*

[32] CHAVANNE, *Compt. rend.*, **158**, 1698 (1914).

[33] *International Critical Tables*, Vol. I, McGraw-Hill Book Co., New York, **1928**.

[34] GLADSTONE, Ph.D. Dissertation, University of Chicago, 1936.

[35] TIMMERMANS, *Bull. soc. chim. Belg.*, **36**, 502 (1927).

[36] DEWAEL, *ibid.*, **39**, 87 (1930).

all the possible addition products. Our constants are compared with those of previous workers in Table VI. Only a few grams of the 1,1-dihalides and of 1-bromo-2-chloropropanes could be obtained by this procedure because of the small quantity of starting materials available, and their indices of refraction are subject to an uncertainty of perhaps ±0.0005, with a corresponding effect on the accuracy (but not the precision) of the composition of the addition products. The probable impurity in the 1,1-dihalides is of course the 1,2-dihalide of higher index of refraction; in the 1-bromo-2-chloropropane, the 2,2-dihalide of lower refractive index.

The side-reaction with ethyl mercaptan.—Experiments 44 in Table IV and 98 in Table III were carried out with 0.100 mole of halopropene in the presence of 0.050 and 0.100 mole of ethyl mercaptan, respectively. In each experiment, in addition to the products noted in the tables, close to 4.0 g. of liquid of b.p. 85–110°/22 mm. was obtained. The two products were almost identical. By qualitative tests, each contained sulfur and bromine but no chlorine. The bromine was easily removable by shaking with excess aqueous alcoholic silver nitrate for two or three minutes, after which no more silver bromide precipitated. Rough titration of the remaining silver nitrate by the Volhard method showed that the substances contained between 25% and 30% of active halogen. (Calc'd for $C_3H_6(Br)SC_2H_5$: Br. 43.7%.) When treated with aqueous alcoholic sodium hydroxide for half an hour at room temperature and then with dilute sodium nitroprusside solution, neither substance gave any indication of the presence of ethyl mercaptan. Hence, we conclude that the bromine and thioethoxyl radicals cannot be on the same carbon atom. The mixtures probably contain the diethyl ether of propylene dithioglycol and a bromopropyl ethyl sulfide, formed by the reaction of 1,2-dihalopropane with ethyl mercaptan and/or the addition of ethyl mercaptan to 1-halopropene. Since halogen and thioethoxyl groups are not on the same carbon atom, the presence of this side reaction has not reduced the proportion of 1,1-dihalopropane formed in the normal addition of hydrogen bromide but may have removed some 1,2-dihalopropane formed by the "peroxide-catalyzed" addition. Further investigation of the by-product was discouraged by the small quantity of material available and its lack of homogeneity.

SUMMARY

1. The "normal" addition of hydrogen bromide to 2-bromo- or 2-chloropropane yields the 2,2-dihalide. The "peroxide-catalyzed" addition yields the 1,2-dihalide.

2. The "peroxide-catalyzed" addition of hydrogen bromide to 1-bromo- or 1-chloropropane gives the 1,2-dihalide exclusively.

3. It is concluded that the "normal" addition of hydrogen bromide to 1-chloropropene gives mostly the 1,1-dihalide while 1-bromopropene gives only about one-third 1,1-dihalide and two-thirds 1,2-dihalide. These results are confirmed by the study of the addition of hydrogen chloride to these unsaturated halides and are explained by the differing directing influences of chlorine and bromine atoms when opposed to a methyl group.

4. A mechanism involving bromine atoms is proposed to explain the "peroxide effect."

5. New physical constants are given for several dihalogenated propanes.

II. THE REACTION OF UNSATURATED HYDROCARBONS WITH SULFINIC ACID

INTRODUCTION

The object of this work was to investigate the reaction of p-toluenesulfinic acid with unsaturated hydrocarbons.

Sulfinic acids bear the same relation to sulfurous acid as sulfonic acids bear to sulfuric acid. The sulfur atom is in an intermediate stage of oxidation. Sulfinic acids may be oxidized to the corresponding sulfonic acids or reduced to mercaptans. They are unstable and undergo an intermolecular oxidation-reduction reaction similar to that of the inorganic sulfites. A convenient method of preparation is the reduction of a sulfonyl chloride by means of zinc dust. Other methods are: the reaction of a suitable Grignard reagent with sulfur dioxide and, in the case of aromatic sulfinic acid, the reaction of sulfur dioxide with a diazonium salt in the presence of copper powder, or the reaction between an aromatic hydrocarbon and sulfur dioxide using aluminum chloride as a catalyst.

Kohler and Reimer[1] have added sulfinic acids to α-, β-unsaturated aldehydes, acids, and ketones but there is no reference of any addition to alkenes. Addition of benzene-sulfinic acid or p-toluenesulfinic acid to cinnamic aldehyde produced a mixture of two sulfones: a monosulfone in which the sulfinic acid had added to the ethylenic double bond, and the disulfone in which a second molecule of sulfinic acid had added to the carbonyl group. Sulfinic acid was also added to the double bond of cinnamic acid, benzalacetone, and to one double bond of dibenzalacetone. The sulfinate ion adds to the β- carbon atom in all cases. For example, the sulfone obtained by the reaction of p-toluenesulfinic acid with cinnamic acid has the structure

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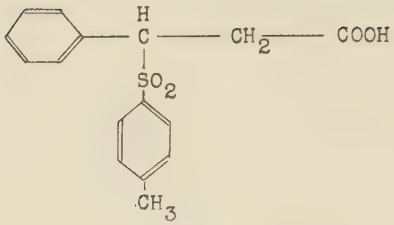
[1]Kohler and Reimer, Am. Chem. J., 31, 163 (1904).



E. May,[2] working in this laboratory, has reinvestigated the addition of sodium bisulfite to allyl alcohol, styrene, propylene, and other unsaturated compounds and has found that the reactions are peroxide-catalyzed. It is believed that the mechanism resembles that proposed on page 11 for the peroxide-catalyzed addition of hydrogen bromide to double bonds and that the ion radical $-(SO_3)^-$ participates in a chain reaction.

As pointed out, the sulfinic acids are chemically related to sulfurous acid and it was attempted to bring about a reaction between allyl alcohol and p-toluenesulfinic acid. However, the results were entirely negative with respect to both allyl alcohol and alkenes. Apparently the addition of sulfinic acid to conjugated systems proceeds through a different mechanism.

EXPERIMENTAL RESULTS

Preparation of para-toluenesulfinic acid.--Para-toluenesulfinic acid was prepared by reducing p-toluenesulfonyl chloride with zinc dust in water. The directions given in "organic syntheses"[3] for the preparation of the sodium salt were followed. The free acid was obtained by dissolving this salt in water and acidifying with dilute hydrochloric acid. The precipitated acid was collected on a filter and purified by a crystallization from water to which a little charcoal had been added. It was dried in vacuo over calcium chloride.

Reaction with styrene.--It was first attempted to add p-toluenesulfinic acid to styrene. This latter material was care-

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[2]Kharasch, May, Mayo. Unpublished work.

[3]H. Gilman, "Organic Syntheses," Collective Vol. I, John Wiley and Sons, New York, 1932, p. 479.

fully purified by several distillations in vacuo. The reaction was first carried out in glacial acetic acid. Equi-molecular portions of sulfinic acid, styrene, and glacial acetic acid were dissolved in a flask by immersion into hot water until a homogeneous solution was obtained. This was set aside. At the end of five hours a fine precipitate separated. This was collected on a filter, washed with glacial acetic acid, and dried. The maximum yield of a large number of experiments did not exceed 10 per cent of the calculated yield assuming that the product consisted of styrene and sulfinic acid in equi-molar proportions. This crude material was insoluble in most organic solvents except acetic acid. It was crystallized from the latter solvent. The product consisted of exceedingly small needles melting at 140°C. Upon standing, a higher melting material resulted. The products obtained from several runs were analyzed for sulfur. The analyses were not constant. The maximum variations were from 14.8 to 17.6 per cent sulfur. The expected product should contain 12.31 per cent sulfur. The residual solution did not yield any other identifiable compounds. It was concentrated by removing as much acetic acid and styrene as possible under reduced pressure. The residue was a gum consisting of polymerized styrene, sulfinic acid, and the decomposition products of that substance. Many experiments of this nature were carried out but different results were not obtained. When the reaction was carried out in vacuo the polymerization of styrene was largely eliminated. The residue then consisted of unreacted sulfinic acid and decomposition products of the latter. Using dioxane as a solvent no precipitate was observed, but upon evaporation a small amount of the substance described above was isolated. The use of a trace of pyridine as a catalyst gave no marked differences in results. Light had no effect upon this reaction.

At the conclusion of these experiments the various products were combined and carefully crystallized using alcohol, acetone, and dioxane as solvents. The resulting material was sublimed in a molecular still. The substance thus obtained melted at 162° C. The analysis gave the following results: sulfur, 16.83 per cent; carbon, 68.93 per cent; hydrogen, 5.48 per cent; oxygen, 8.76 per cent. The empirical formula calculated from these figures is $(C_{11}H_{10}SO)_x$. Molecular weight determinations indicated a molecular weight of 750. This was determined from both the de-

pression of the melting point of camphor and the elevation of the boiling point of acetone. The molecular weight indicates that "x" of the above formula should be 2. The formula $(C_{11}H_{10}SO)_2$ corresponds to a molecular weight of 760.03. No plausible structure can be assigned to this formula. The fact that the sulfur to oxygen ratio is one to one shows that straight addition had not taken place. One of the decomposition products of sulfinic acid may have reacted with styrene. No chemical tests were carried out since only a few milligrams were left after the final purification.

There are two complications that one must bear in mind in carrying out the reaction between sulfinic acid and styrene. All sulfinic acids are relatively unstable. In solution and even in the dry state they undergo the following intermolecular oxidation-reduction reaction:

$$3\ R\text{-}SO_2H \rightarrow R\text{-}SO_2\text{-}S\text{-}R + R\text{-}SO_3H + H_2O$$

Secondly, styrene readily polymerizes when exposed to air. The rate of decomposition of sulfinic acid seems to outrun the rate of addition. The nature of the reaction mixture makes it impossible to isolate small quantities of the expected products should they be formed. No disulfoxide $R\text{-}SO_2\text{-}S\text{-}R$[4] was isolated although it was probably present.

Reaction with trimethylethylene and isobutylene.--The reaction of sulfinic acid with trimethylethylene and isobutylene was also studied. The conditions were similar to those held previously; except that no precautions were necessary with these hydrocarbons to avoid polymerization. No addition products were found with these substances under a variety of conditions. The end product of the reaction was a mixture of the disulfoxide, unreacted sulfinic acid, unsaturated hydrocarbon, and a trace of an oily material. From the odor of the latter one might surmise that the material was an alcohol. No further identification, however, was attempted.

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[4]These compounds are commonly known as disulfoxides since they were assigned the structure R-SO-SO-R by Otto and Schiller, Ber., 9, 1636 (1876). Hinsberg, Ber., 41, 2836, 4294 (1908), has presented much chemical evidence to support this view. Lately, however, the formula R-SO2-S-R has received strong support from the work of Smiles and Gibson, J. Chem. Soc., 125, 176 (1924) and Gilman, Smith, and Parker, J. Am. Chem. Soc., 47, 851 (1925). Hence the disulfoxides should be regarded as esters of thiosulfonic acids, $R\text{-}SO_2\text{-}SH$.

Titration of sulfinic acid.--To follow the course of the reaction of sulfinic acid and unsaturated compound in neutral solvent, samples of the reaction mixture containing dioxane were withdrawn at frequent intervals and titrated with sodium hydroxide, using phenophthalein as an indicator. Since the amount of sulfinic acid titrated decreased from one interval to the next, either addition or decomposition had taken place. To distinguish between these two possibilities a second reaction mixture not containing any unsaturated compound but otherwise identical with the first was titrated simultaneously. The titers were always identical, within the limits of experimental error, showing that no addition had taken place. This method can be utilized only with a neutral solvent.

Para-toluenesulfinic acid is oxidized instantaneously to the sulfonic acid whereas acetic acid is oxidized very slowly. Using this observation, reaction mixtures containing camphene, the only unsaturated hydrocarbon available which did not react rapidly with potassium permanganate, showed the same rate disappearance as reaction mixtures not containing camphene. Again, no addition seems to have taken place. Fifty per cent of the sulfinic acid decomposed in four days. All reaction mixtures were kept at room temperature.

Reaction with allyl alcohol.--It was also attempted to add p-toluenesulfinic acid and its sodium salt to allyl alcohol. The allyl alcohol used was the practical grade containing about 30 per cent water and was purified by distillation in vacuo. A reaction mixture consisting of sulfinic acid and aqueous allyl alcohol in the mole ratio of three to one was prepared. This was heated to 60°C. for forty-eight hours. Over 90 per cent of unchanged sulfinic acid was recovered. When the sodium salt was used the result was quite similar. Neither did a slow stream of oxygen or a trace of cupric ion produce any demonstrable catalytic effect.

SUMMARY

The reaction of p-toluenesulfinic acid with a number of alkenes and allyl alcohol was investigated to determine if addition takes place. No addition was observed.

The author wishes to express his sincere gratitude and appreciation to Professor M. S. Kharasch and Dr. F. R. Mayo for their help and guidance during this investigation.